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SOME OCTA (4-ACETAMEDO) TETRAPYRAZINO PORPHYRAZINE COMPLEXES AND THEIR SPECTROSCOPIC AND ELECTRICAL PROPERTIES

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ABSTRACT

A coplexes of octa (4-acetamidophenyl) octaazaphthlocyaninato Zinc and Copper (11) were prepared and identified. The study shows some of their spectroscopic and electrical properties. It shows too, the effect of solvents on the electronic spectra. The dc electrical conductivity measurements show their semiconducting properties.

KEYWORDS: Organic Experiments, Coordination Chemistry, Phthalocyanine

INTRODUCTION

Porphyrazins or tetraazaporphyrins are divided into two main groups, phthalocyanines (Pc) and Azaphthalocyanines (AzaPc)[(1)].

Due to their unique electronic and optical properties, they have potential application as biomedical agents, chemical sensors, liquid crystals and non-linear optical materials[(2,3)].

Recently, porphyrazins have gained increasingly attention. This is due to the strong correlation between the nature of the substituents with the electronic and optical properties of the macro cyclic ring system[(2)].

The Azaphthalocyanines show good solubility in organic solvent compared to phthalocyanine complexes[(4)]. Due to the extended π-conjugated system in phthalocyanine and Azaphthalocyanines, they exhibit a high tendency for aggregation, which causes the decrease of solubility and difficulty of purification and characterization in addition to the broadening of Q-band and the low ability to generate the singlet oxygen which is the active agent in photodynamic therapy (PDT)[(5)]. The dc electrical studies show a semiconducting properties. In this work a complexes of octa (4-acetamedophenyl) tetrapyrazino porphyrazine with Cu and Zn as central metal atoms were prepared and characterized by CHN, IR, U. V-Visible and H-NMR. The dc electrical properties and the effect of different solvents on the electronic spectra for the prepared compounds were studied.

EXPERIMENTAL SECTION

Materials

The purchased chemicals were used as they were received. Ethanol, acetone and chloroform were purchased from GCC. Potassium cyanide, Zinc chloride, Dimethyl sulphoxide (DMSO) and HNO_3 were purchased from BOH. HAc, Copper Nitrate, diaminomalonitril (DAMN), Quinoline, pyridine, and urea were purchased from RDH and hexanol, Silica gel and Iodine were purchased from Merck.

Instrumentation

The elemental analysis were recorded on CHNS-O Perkin Elemer, model 2400-11. The IR spectra were recorded on FT- IR – 8400S. The UV-Visible spectra were recorded for solution of 10^{-5}M DMSO on UV-2100 PC spectrophotometer.

The ^{1}H-NMR (300MHz) spectra were recorded by Bruker. The dc electrical conductivity measurements were performed using an electrical circuit containing power supply (Leybold Heraeus), heating plate (TJLASSO) and avometer (DT890).

The cells were prepared by casting a concentrated solution of any of the compounds in DMF on a smooth and well cleaned aluminum surfaces as electrodes.

PREPARATION OF THE COMPOUNDS

- **Preparation of 4,4'-Diacetamidobenzoin[6]**

A 0.248g (3.875×10^{-3}mol) of Potassium cyanide was dissolved in 4 ml of distilled water and added to a 100 ml conical flask, fitted with condenser, containing 4g (2.46×10^{-2} mol) 4-acetamidobenzalde-hyde soluble in 8 ml of ethanol. The mixture then refluxed for 2 hours[126]. The reaction mixture then left to be cooled, Then added portion wise with stirring to a 200 ml beaker containing 50 ml of distilled water. A solid was precipitated, filtered and re-crystallized from chloroform and then dried at 100 °C. The product was orange powder, yield (1.8g, 45%).

- **Preparation of 4,4'- Diacetamidobenzil (PAcBz)[6]**

A mixture of 4g (12.27×10^{-3}mol) of 4,4'- diacetamido benzoin and 14 ml of concentrated nitric acid were heating in conical flask on the steam bath for 18 min until the removal of the brown nitrogen oxide fumes then added 75 ml of water to the reaction mixture and cooled to room temperature and left for a minute to coagulate the precipitated product, then the brown solid collected and washed with distilled water on Buchner funnel then re-crystallized from ethanol and purified by column and dried at 100 °C. The product was brown powder, yield (3.2g, 58%).

- **Preparation of 2,3-Dicyano-5,6-Bis (4-Acetamidophenyl) Pyrazine (PAcPN)[7]**

A 1g (3.1×10^{-3} mole) of 4,4'- diacetamido benzil was dissolved in a mixture of 25 ml of ethanol and 25 drops of acetic acid and then added to conical flask containing (0.334 g, 3.1×10^{-3}mol) of diaminomalo nitril (DAMN) soluble in 25ml of ethanol. The total mixture then refluxed for 4.5 hours. The reaction mixture then left for two days to complete the precipitation. The solid product then filtered and re-crystallized from a mixture of hexanol and acetone (1:1). Then filtered and dried. The product is brown powder, yield (0.88g, 72%).

- **Preparation of 2,3,9,10,16,17,23,24- Oct (4-Acetamidophenyl)-1,4,8,11,15,18,22,25–Octaazaphthlocyaninato Copper (II) (PAcPzCu)[8]**

A 0.117 g (6.3×10^{-4}mole) of copper nitrate was added to a solution of 1g (4×10^{-3} mole) of PAcPN in 3 ml of quinoline (distilled). A1.2 gm (2×10^{-2} mole) of urea were added to the mixture and the mixture was heated to 140°C with magnetic stirring for 15 minutes and the reaction mixture then cooled and filtered. The solid product dissolved in a least amount of chloroform and re precipitated by adding it portion wise with stirring to a beaker containing 200 ml ethanol. The precipitation process was repeated for three times, and then dried at 120 ºC. The product is a brown powder, yield (0.7g, 67.4%).

CHN, calcd ($C_{88}H_{64}N_{24}O_8Cu$) C: 64.085, H: 3.91, N: 20.38; found C:63.30, H: 3.01, N:20.28.

- **Preparation of 2,3,9,10,16,17,23,24- Oct (4-Acetamidophenyl)-1,4,8,11,15,18,22,25–Octaazaphthlocyaninato Zinc (II) (PAcPzZn)[8]**

A 0.103 g (6.3×10^{-4}mole) of Zinc Chloride was added to a solution of 1g (4×10^{-3} mole) of PAcPN in 3 ml of quinoline (distilled). A 1.2 gm (2×10^{-2} mole) of urea was added to the mixture, The mixture then heated to 140°C with

magnetic stirring for 15 minutes. The reaction mixture was cooled and filtered. The solid product then dissolved in a least amount of chloroform and re precipitated by adding it portion wise with stirring to beaker containing 200ml ethanol. The precipitation process was repeated for three times, and then dried at 120 ºC, The product is a red powder (yield, 0.57 g, 54.8 %).

CHN, calcd ($C_{88}H_{64}N_{24}O_8Zn$) C: 64.01, H: 3.9, N: 20.36; found C: 63.50, H: 4.39, N: 19.77.

RESULTS AND DISCUSSIONS

The little differences of the practical with the calculated elemental percentage in the CHN analysis might be due to the difficulties of purification of such compounds.

The figures 1, 3 show the IR spectra of PAcPN and its complexes PAcPzCu and PAcPzZn respectively. It shows the aromatic C-H stretching at 3190 cm $^{-1}$, 3210 cm^{-1} and 3200 cm^{-1}for the compounds respectively and the aromatic C-H bending at 839 cm^{-1}, 952cm^{-1} and 955 cm^{-1} in plane for them respectively, and 669 cm^{-1},808 cm^{-1} and839 cm^{-1} out of plane respectively.

The bands 1384cm^{-1}, 1375cm^{-1} and 1373cm^{-1} are for the respective compounds attributed to the stretching vibration for C-N, and the bands 1683 cm^{-1}, 1670 cm^{-1} and 1685 cm^{-1} are attributed to the stretchy vibration for C=N respectively, and C≡N stretchy vibration for PAcPN at 2214 cm^{-1}[9-11].

The bands 3348 cm^{-1}, 3331 cm^{-1} and 3317 cm^{-1} are attributed to the stretchy vibration for N-H respectively.

The IR spectrum showed the specific bands of the porphyrazines. The PAcPN show the C≡N band which is disappeared in porphyrazines.

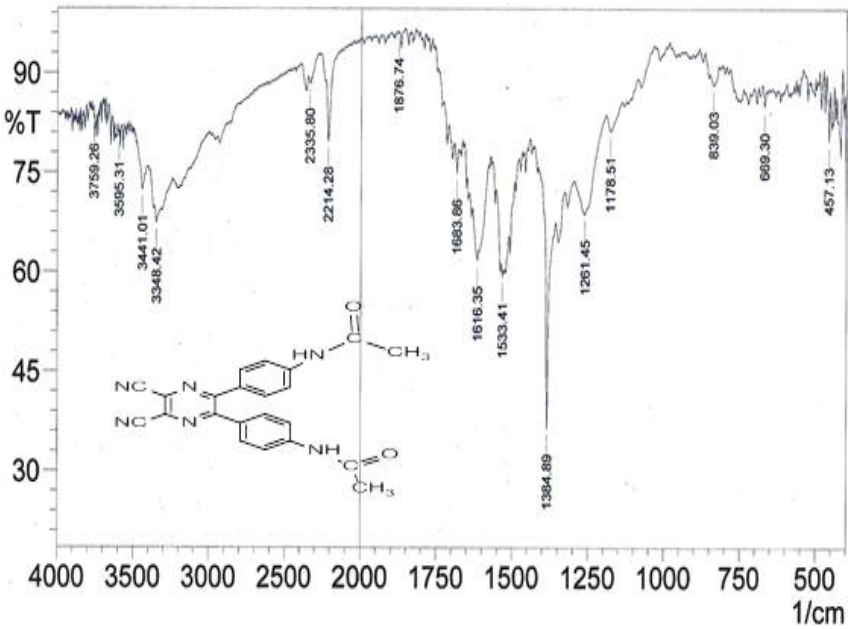


Figure 1: The IR Spectrum of PAcPN

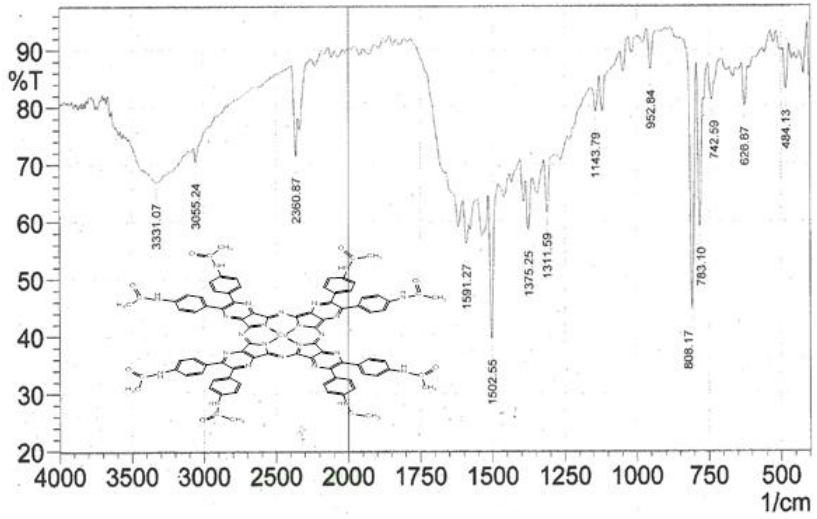


Figure 2: The IR Spectrum of PAcPzCu

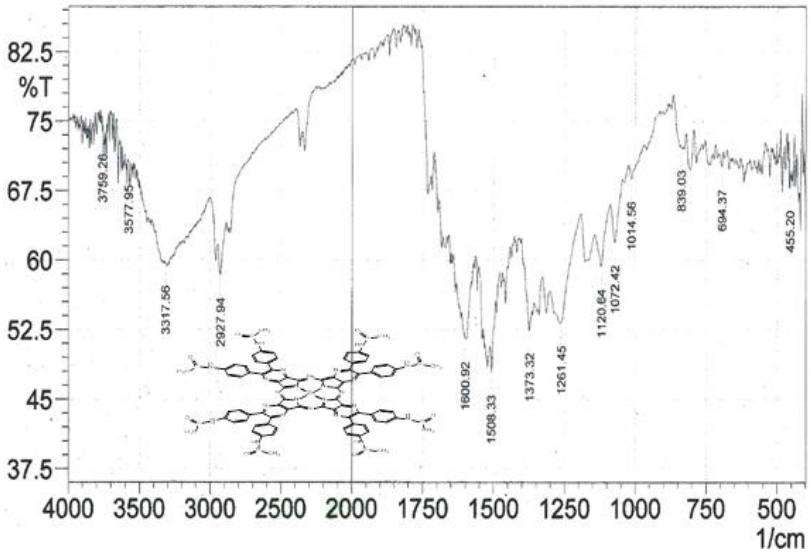


Figure 3: The IR Spectrum of PAcPzZn

The U.V-Visible spectra, figures 4 and 5, show the two main bands, at 651 nm and 636 nm (Q band) and 345 nm and 340 nm (soret band) for PAcPzCu and PAcPzZn complexes respectively, Which could be attributed to the π-π^* transitions in addition to the n-π^* coupling of electrons of the nitrogen atoms to the π-system[12-15].

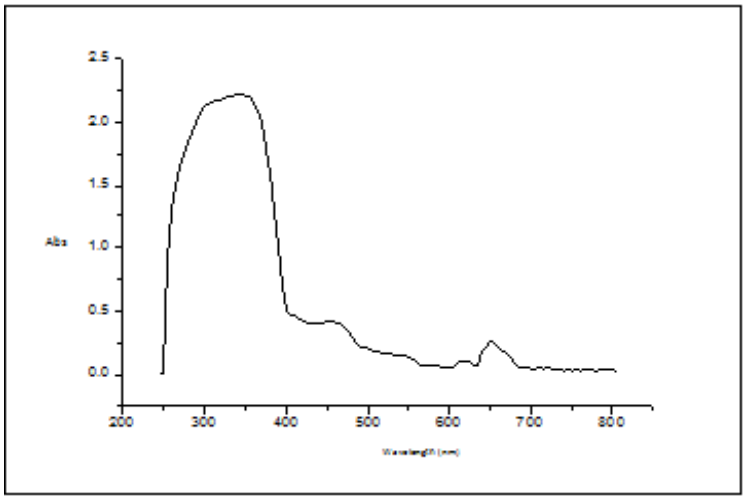


Figure 4: The U.V-Visible of PAcPzCu

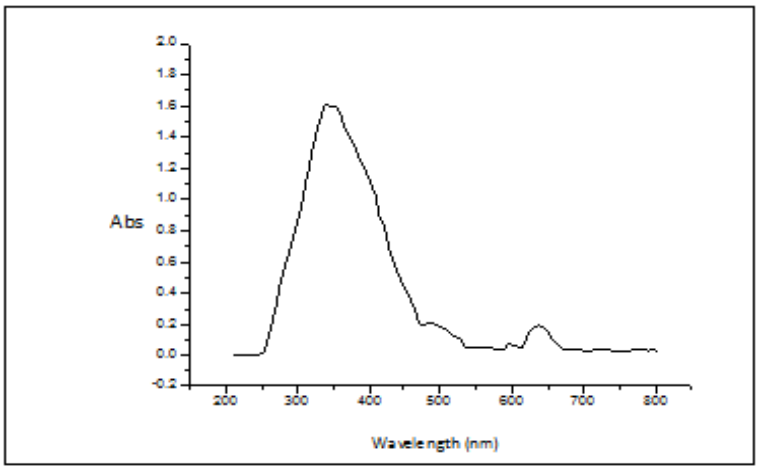


Figure 5: The U.V-Visible of PAcPzZn

The ^{1}H NMR spectrum, figure 6 and 7 shows a mixed bands at 7.8 ppm and 8 ppm for the PAcPzCu and PAcPzZn complexes respectively, which could be attributed to the benzene protons, while the beaks at (2.491, 3.348 ppm) and (2.485, 3.340 ppm) are attributed to the solvent DMSO and absorbed water for the two complexes respectively, and the beaks at 2.1 ppm and 2.05 ppm related to the methyl protons for the two complexes respectively, while the beaks at 5.5 ppm 5.404 ppm is attributed to the N – H proton for the two complexes respectively[16].

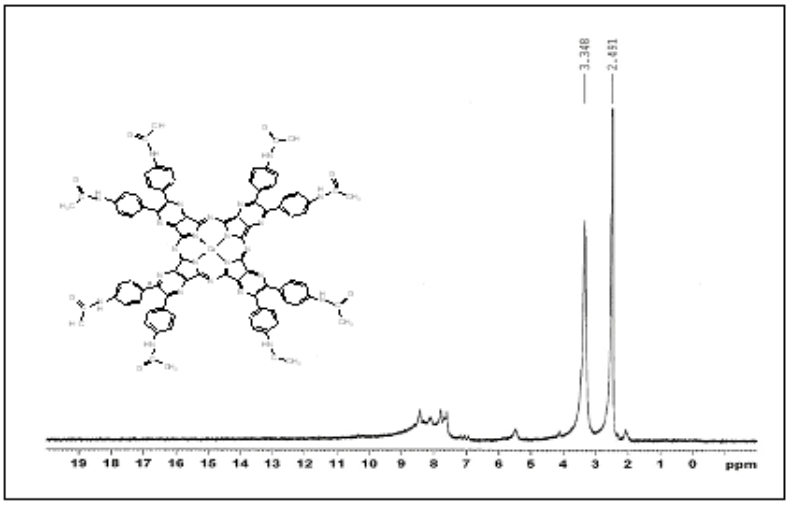


Figure 6: The ^{1}H-NMR Spectrum of PAcPzCu

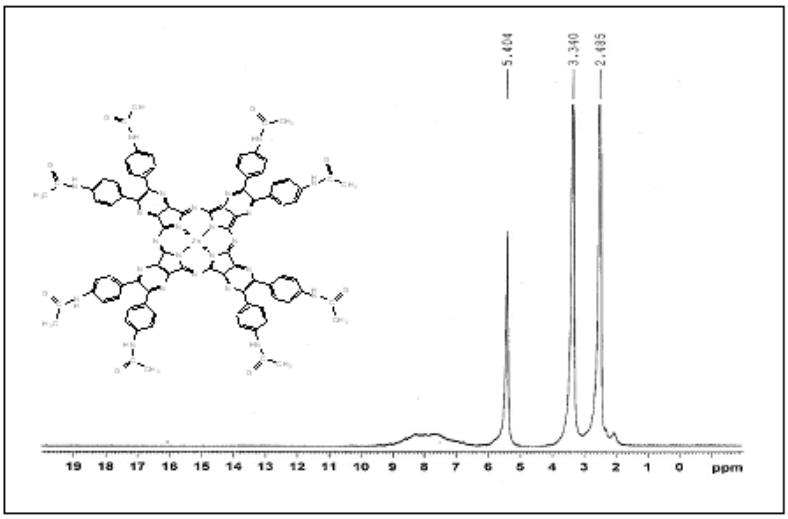


Figure 7: The H-NMR Spectrum of PAcPzZn

Effect of the Solvents Shows of on the Electronic Spectra

The study shows that the kind of the solvent has effect on the shape and position of the main peaks. In the high polarity solvents, such as, pyridine, DMF and DMSO, the Q band shows one sharp beak which refers to the D_4h symmetry. The less polar solvents such as Toluene, chloroform and THF show a wide Q bands which refer to the lower symmetry due to the aggregation of the Porphyrazine molecules[17-20].

The presence of extra nitrogen atom in the Porphyrazine makes it more polar which leads to the aggregation of the porphyrazine molecules[21].

The polar nitrogen atoms makes the central atom more acidic which could be attached to the central metal atoms then leads to reduce the aggregation[19-20].

The study shows that using of pyridine as solvent for the prepared complexes, the hight of Q band increases with time till the system reach to an equilibrium during about 2 hours.

Figures 7 and 8 show the UV-Visible spectra (Q band) for the PAcPzCu and PAcPzZn complex at (655 and 637) nm in pyridine respectively with the time, from lower to higher peak.

The width of the peak refers to the aggregation of the molecules[22].

In pyridine the peaks become higher and extra thinner with the time which could make extra coordination with the central metal atoms that reduce the aggregation[20]

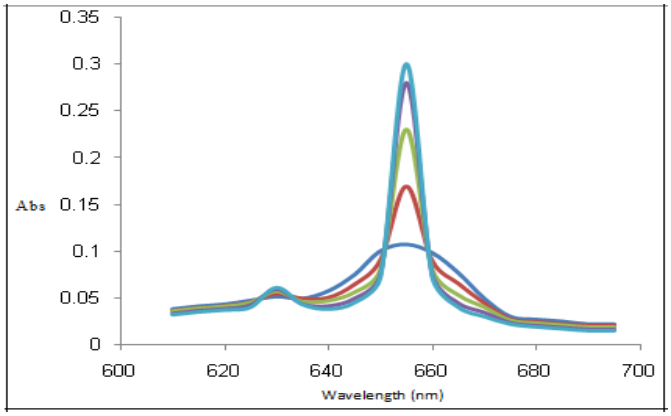


Figure 8: The U.V-Visible Spectra of PAcPzCu Complex in Pyridine with Time at 655 nm Upwards 1) 5 min 2) 15 min 3) 30 min 4) 60 min 5) 90 min

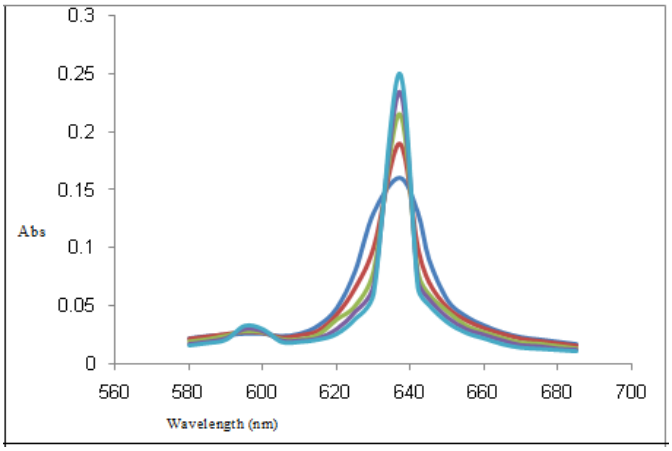


Figure 9: The U.V-Visible Spectra of PAcPzZn Complex in Pyridine with Time at 637 nm Upwards 1) 5 min 2) 15 min 3) 30 min 4) 60 min 5) 90 min

The reaction of the complex with pyridine could be explained:

$PAcPzCu + nPy \rightleftharpoons PAcPzCu(Py)_n$

(n) is the number of moles of pyridine.

The equilibrium constant K:

$$\frac{[PAcPzCu(Py)_n]}{[PAcPzCu][Py]^n} \quad (1)$$

n and k could be calculated from the follows equation [23,24,2] :

$$K = \frac{D-D_\circ}{D_\infty-D} \times \frac{1}{[Py]^n} \quad (2)$$

$$\ln K = \ln\frac{D-D_\circ}{D_\infty-D} - n\ln[Py] \quad (3)$$

$$\ln\frac{D-D_\circ}{D_\infty-D} = \ln K + n\ln[Py] \quad (4)$$

when D_o, D_∞ and D are optical densities of the complexes before the addition of pyridine, at the pyridine concentration, and in equilibrium respectively.

Figures 10 and 11 show the variation of the Q beak with concentration of the complexes PAcPzCu and PAcPzZn respectively.

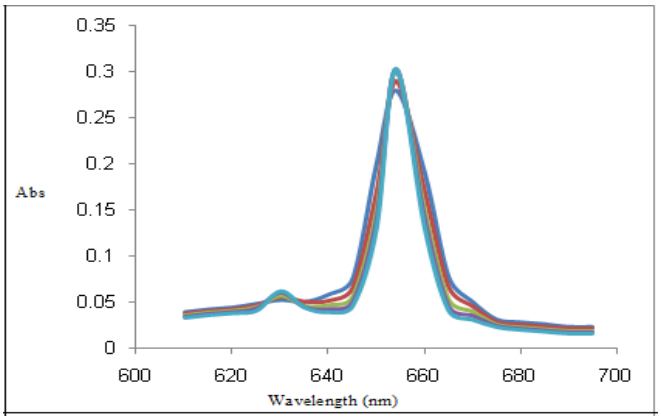


Figure 10: Variation of the Q Band of the PAcPzCu in Chloroform with a Complex Complex Concentration of 1x10 $^{-5}$ M with Different Concentration of Pyridine (1,2,4,8)10^{-5}

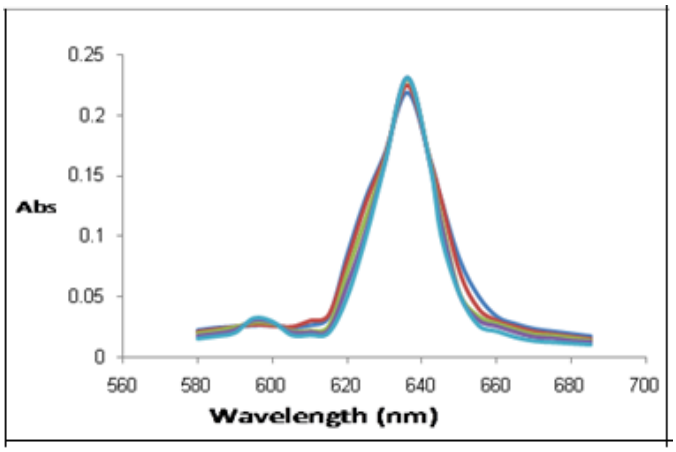


Figure 11: Variation of the Q Band of the PAcPzZn in Chloroform at a Complex Concentration of 1x10 $^{-5}$ M with Different Concentration of Pyridine (1, 2, 4,8) ×10^{-5} M

Plotting ln [(D-D_0)/(D_∞-D)] with ln [Py]is shown in figures 12,13:

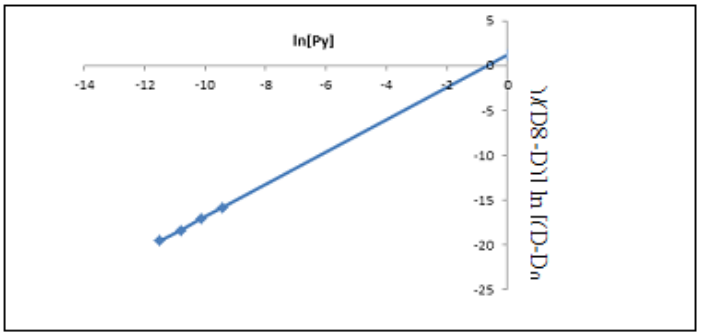


Figure 11: Variation of the [(D-D_0)/(D_∞-D)] with in [Py] for the PAcPzCu Complex

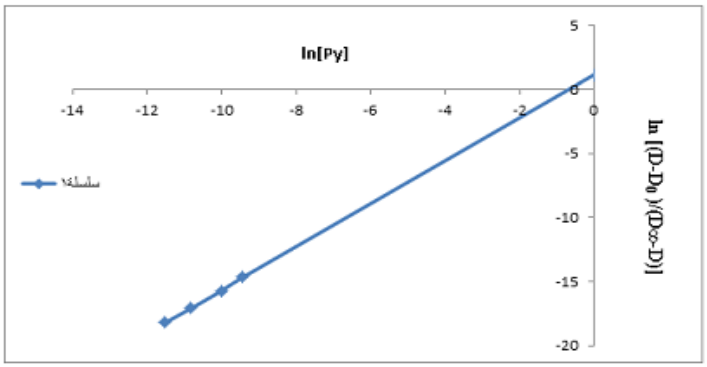
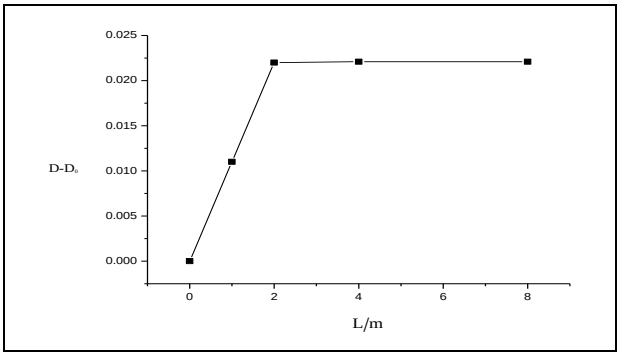


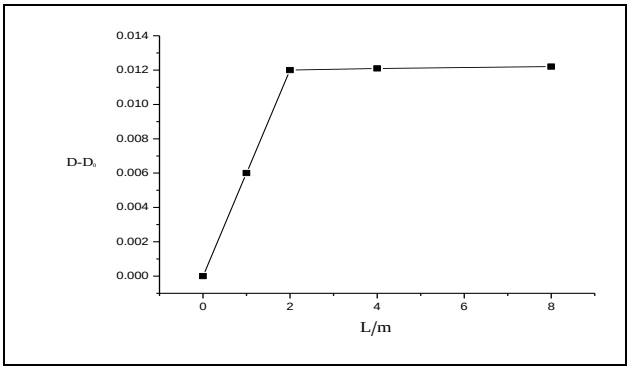
Figure 12: Variation of the [(D-D_0)/(D_∞-D)] with in [Py] of the PAcPzZn Complex

The slopes of the graphs = the number of pyridine molecules attached to the central metal atoms (n).

Figures 12 and 13 show the relative of D-D_0 with L / m:



Figures 12: The Relation of D-D_0 with L / m for the PAcPzCu Complex



Figures 13: The Relation of D-D_0 with L / m for the PAcPzZn Complex

The graphs show the attachments of 2 pyridine molecules with central metal atoms for both complexes.

From the graphs 12 and 13 and equation 2 we can calculate K. It's calculated values are 3.3 and 3.1 for cu and zncompleses.

From the Equation: $\Delta G = - RT \ln K$ (5)

ΔG is calculated. It's values are -2958.2 J/mol and -2803.29 J/mol for the cu and complexes respectively at 25˚C.

The Electrical Properties

The D.C electrical measurement were carried out using a sandwich thin films casted in between electrods. The measurements were carried out by a circuit consists of power supply.

Figures 14 and 15 show the variation of current with voltage for PAcPCu and PAcPZn Respectively in the voltage range (1-60) volts and the temperature range (25-75) ^{0}C.

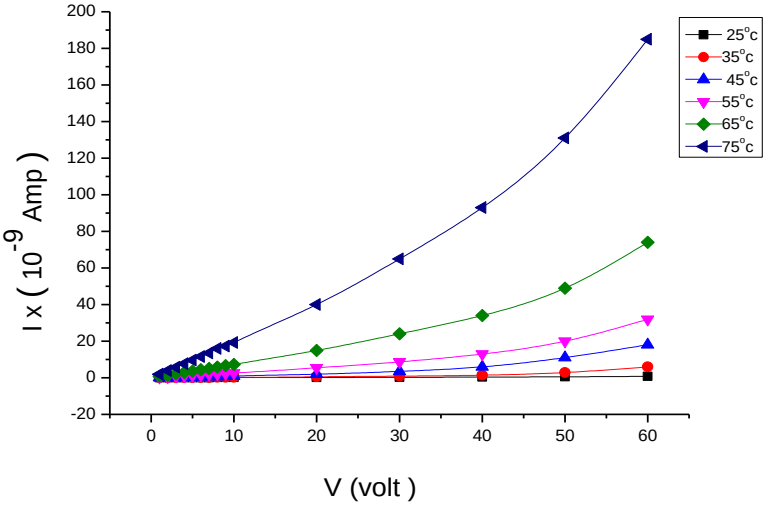


Figure 14: The Current Voltage Relation foPAcPzCu Complex

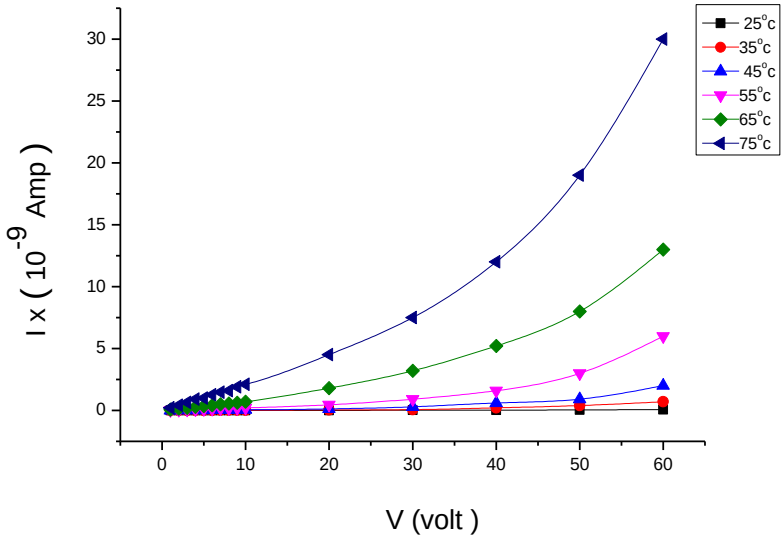
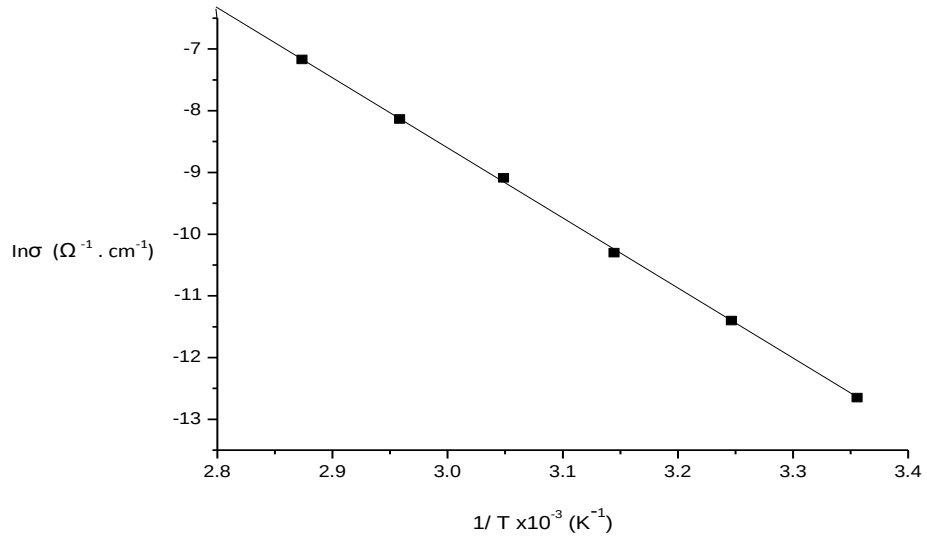


Figure 15: The Current Voltage Relation of PAcPzZn Complex

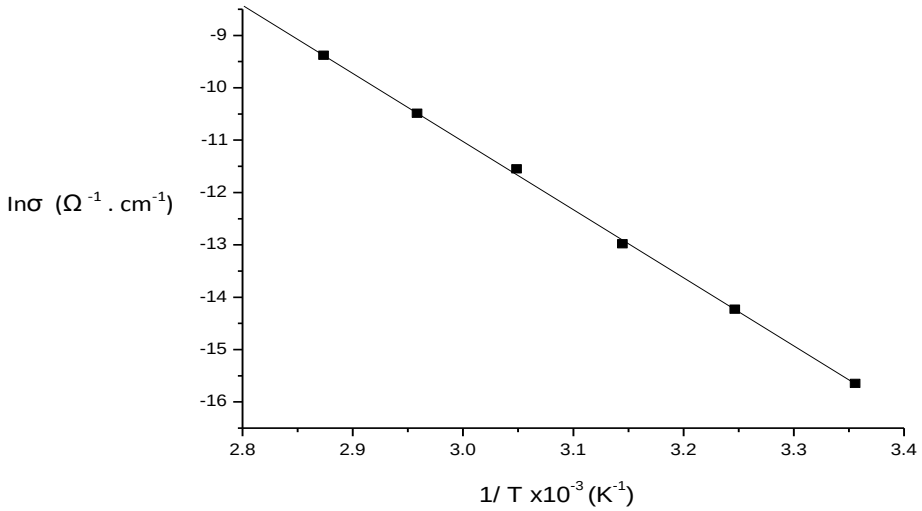
The figures show the ohmic relation in the rang (1-10) volts in the studying temperature range. At higher voltages the relation become non ohmic due to the effect of space charge limited current (SCLC)[(25)].

Applying Arrhenius equation, $\sigma = \sigma_o \exp(-\Delta E / kT)$[26], where σ is the conductivity of the cell, σ_o is the pre-exponential factors, ΔE is the Activation energy, K Boltzmann constant, T temperature in Kelvin.

Figures 15 and 16 shows the relation between$\ln\sigma$ and 1/T for both complexes PAcPzCu and PAcPzZn respectively.



Figures 15: The Relation between lnσ and 1/T for PAcPzCu Complex



Figures 16: The Relation between lnσ and 1/T for PAcPzZn Complex

The slopes of the graphs is $\Delta E/k$.

Table 1: The ΔE and σ_o for Both Complexes

Compound	ΔEEV	$\Omega^{-1}Cm^{-1}\sigma$
PAcPzCu	0.977	1.74 x 10-3
PAcPzZn	1.12	2.25x 10^{-4}

The low vales of ΔE refers to the presence of impurities, so the ΔE refers that the conductivity is notextrinsic.

The Table shows that PAcPzCu is of higher conductivity.

The differences in conductivities could be explained as a Results to the differences in the size of central metal atoms and the nature of packing and impurity[27-29].

REFERENCES

1. A. Ghosh, J. Fitzgerald, P.G. Gassman, and J. Almof, "*Inorg. Chem*", 33, 6057-6060, **(1994).**
2. E. Gonca., Highly symmetrical polyfluorinatedporphyrazines., "J. fluorochem"., 149.65-71 **(2013)**.
3. J. M. Fox.; T.J. Katz.; S, Van Elshocht.; T, Verbiest.; M, Kauranen.; A. Persoons.; T,; Krauss, T. Thongpanchang.; and L. Brus.; J. AM. Chem. Soc. 121, 3453-3459**(1999**).
4. M. P. Donzello, C. Ercolani and P. A.Stuzhin, *"Coordination Chemistry Reviews*", 250, 1530 **(2006)**.
5. M. Kostka., P. Zimcik., M. Miletin., P. Klemera., K. Kopecky and Z. Musil., *"J. photochem. Photobiol, A-Chem"*. 178, 16-25**(2006**).
6. L.F. Fieser and K L. Williamson. ; "*Organic Experiments*" D.C. Heath and Company PP. 263-264.(**1974**).
7. H. I. Ugras, I. Basaran, T. Kilic, U. Cakir, *J. Heterocyclic Chem.*, 43, 1679**(2006)**.
8. R. Faust and C. Weber, J. Org. Chem., 64(7) 2571 **(1999).**
9. C. Bergami, M. P. Donzello, C. Ercolani, F. Monacelli, K. M. Kadish and C. Rizzoli, lnorg. Chem., 44, 9852 **(2005)**.
10. S. Makhsee, J. Samuel and F. Ibrahim, *Tetrahedron*, 64, 8871**(2008)**.
11. G. Socrates, "*Infraed Characteristic Group Frequecies*" John Wiley Sons, Ltd, New York, Copyright **(1980)**.
12. A. S. T. Al Salami, "M.Sc. Thesis" University of Basrah, Iraq, (**2009**).
13. F. H. H.Alkhafa,"M.Sc.Thesis" University of Basrah,Iraq, (**2012**).
14. M. Bauer, M. Feth, V. Krishnan, H. Bertagnolli," Applications of Ezafs Spectroscopy-from Materials Chemistry to Catalysis", Hasylabxafsstatellite meeting **(2005).**
15. S. J. Tans, L. J. Geerligs and C. Dekker, *J. Vac. Sci, Technol*, B15(3)**(1997).**
16. R. M. Silverstein and F.X-Webster, "*Spectroscopic Identification of Organic Compounds*", 6th Ed, John Wiley and Sons, Inc.,New York **(1996)**.
17. M. P. Donzello, D. Dini, G. D'Arcangelo, C. Ercolani, R. Zhan, Z. Ou, P. A. Stuzhin and K. M. Kadish, *J.Am. Chem. Soc*., 125, 14190 **(2003)**.
18. C. K. Jang and J. Y. Jaung, *Materials Letters*, 62, 3209 **(2008)**.
19. F. H. Moser and A. L. Thomas, *"phthalocyanine compounds*", Reinhold publishing corpbration, New York**, (1963)**.
20. K. Kopecky, p. Zimcik, V. Novakova, M. Miletin, Z. Musil, *J. Stribna, Dyes and Pigments,* 78, 231 **(2008).**
21. C. Zhong, M. Zhao, T. Goslinski, C. Stern, A. G. M. Barrett and B. M. Hoffman, *lnorg. Chem*., 45, 3983 **(2006)**.
22. P. Zimicik., M. Miletin., Z. Musil, K. Kopeeky., L. Kubza and D. Brault., *J. Photochem. Photobiol. A-Chem.*, 183, 59-69 (**2006)**.
23. O.I. Koifman, T.A. Koroleva and B.D.Berezin, *Soviet J. Coord. Chem.*, 3(12), 1420 **(1977)**.
24. S.F.Ginzburg, L.P. Brinina, G.V. Ponomarev and V.V. Khrapov, *Soviet J. Coord. Chem.*, 3(12), 1394 **(1977)**.

25. D. Weuive and M. F. Thorpe, *Phys. Rev*., 4, 2508 **(1971)**.

26. M. P. Donzello et al., *Inorg. chem*., 43(26), 8626 (**2004**).

27. J. P. Linsky and T. R. Paul., *Inorg. Chem*., 19, 3131, **(1980)**.

28. M. Futamata, S. Higuchi and S. Takahashi., *Synth. Met*., 30, 39, **(1989)**.

29. N. A. Hussein., Ph. D. thesis, Nottingham University, **(1990)**.